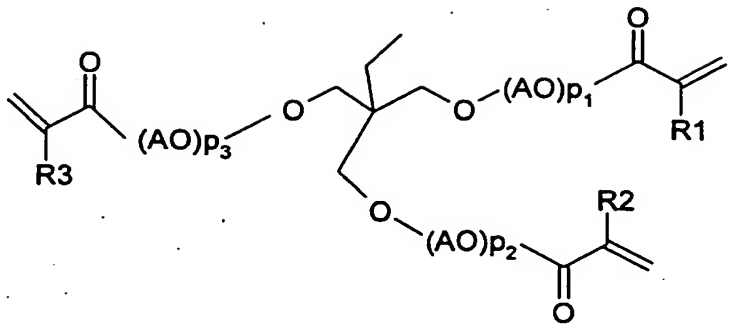
We claim:-

1. An ester F of the formula I a



where AO is for each AO independently at each instance EO, PO or BO

where EO is O-CH2-CH2-

PO is independently at each instance O-CH2-CH(CH3)- or O-CH(CH3)-CH2-

BO is independently at each instance O-CH2-CH(CH2-CH3)- or O-CH(CH2-CH3)-CH2-

p1 + p2 + p3 is 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74 or 75,

R1, R2 and R3 are independently H or CH3.

2. An ester F as per claim 1, wherein at least one AO is EO and at least one further AO is PO or BO.

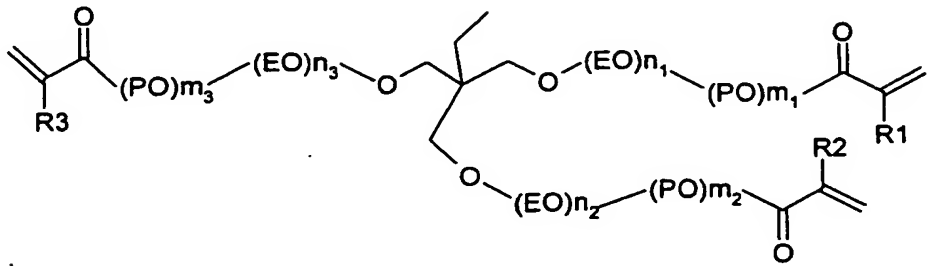
3. An ester F as per either of claims 1 and 2, wherein AO is EO in at least half of all instances of AO.

4. An ester F as per any of claims 1 to 3, wherein only PO or BO is present as well as EO.

5. An ester F as per any of claims 1 to 4, wherein there are present n1 + n2 + n3 EOs with n1 + n2 + n3 equal to 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40,

41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59 or 60 and m1 + m2 + m3 POs or BOs with m1 + m2 + m3 equal to 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13.

6. An ester of the formula I b



where EO is O-CH2-CH2-

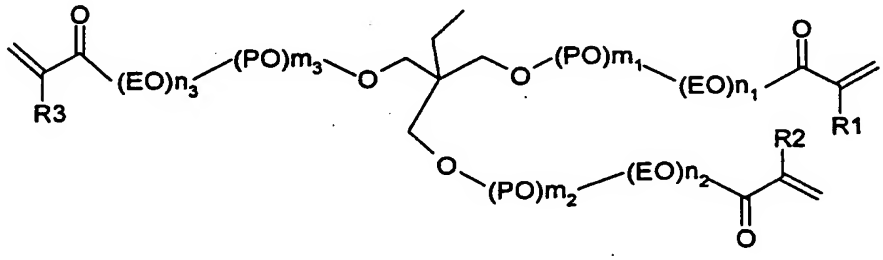
PO is independently at each instance O-CH2-CH(CH3)- or O-CH(CH3)-CH2-

n1 + n2 + n3 is 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59 or 60,

m1 + m2 + m3 is 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13,

R1, R2 and R3 are independently H or CH3.

7. An ester F of the formula I c



where EO is O-CH2-CH2-

PO is independently at each instance O-CH2-CH(CH3)- or O-CH(CH3)-CH2-

n1 + n2 + n3 is 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59 or 60,

m1 + m2 + m3 is 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13,

R1, R2 and R3 are independently H or CH3.

8. An ester F as per any of claims 1 to 7, wherein n1, n2 and n3 are independently 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20.

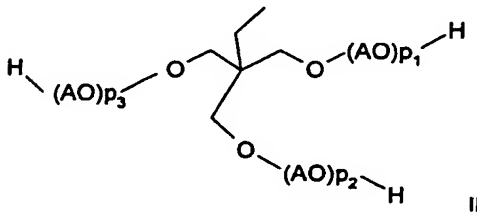
9. An ester F as per any of claims 1 to 8, wherein m1, m2 and m3 are independently 1, 2, 3, 4 or 5.

10. An ester F as per any of claims 1 to 9, wherein m1 + m2 + m3 is 5 or 10.

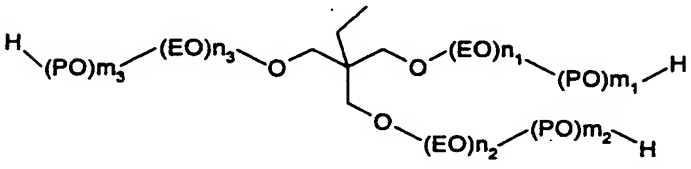
11. An ester F as per any of claims 1 to 10, wherein n1 + n2 + n3 is 30 or 50.

12. An ester F as per any of claims 1 to 11, wherein R1, R2 and R3 are identical and preferably H.

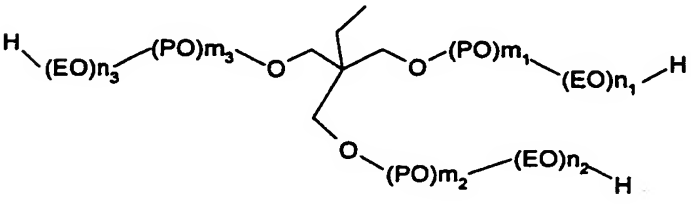
13. A process for preparing an ester F as per any of claims 1 to 12 of alkoxylated trimethylolpropane of the formula II a, II b or II c



II a



II b



II c

where AO, EO, PO, p1, p2, p3, n1, n2, n3, m1, m2 and m3 are each as defined in any of claims 1 to 12,

with (meth)acrylic acid, comprising the steps of

a) reacting alkoxylated trimethylolpropane with (meth)acrylic acid in the presence of at least one esterification catalyst C and of at least one polymerization inhibitor D and optionally also of a water-azeotroping solvent E to form an ester F,

b) optionally removing from the reaction mixture some or all of the water formed in a), during and/or after a),

f) optionally neutralizing the reaction mixture,

h) when a solvent E was used, optionally removing this solvent by distillation, and/or

i) stripping with a gas which is inert under the reaction conditions.

14. A process as claimed in claim 13, wherein

- the molar excess of (meth)acrylic acid to alkoxylated trimethylolpropane is at least 3.15:1 and
- the optionally neutralized (meth)acrylic acid present in the reaction mixture after the last step substantially remains in the reaction mixture.

15. A process as claimed in either of claims 13 and 14, wherein the (meth)acrylic acid is not more than 75% by weight removed from the reaction mixture obtained after the last step, which reaction mixture contains ester F.

16. A process as claimed in any of claims 13 to 15, wherein the reaction mixture obtained after the last step, which contains ester F, has a DIN EN 3682 acid number of at least 25 mg of KOH/g.

17. A process as claimed in any of claims 13 to 16, wherein the reaction mixture obtained after the last step, which contains ester F, has a (meth)acrylic acid content of at least 0.5% by weight.

18. A process as claimed in any of claims 13 to 17, wherein the molar ratio of (meth)acrylic acid to alkoxylated trimethylolpropane in reaction a) is at least 15:1.

19. A process for preparing a crosslinked hydrogel, comprising the steps of

k) polymerizing an ester F as per any of claims 1 to 12, with (meth)acrylic acid, with optionally additional monoethylenically unsaturated compounds N and optionally also at least one further copolymerizable hydrophilic monomer M

in the presence of at least one free-radical initiator K and optionally of at least one grafting base L,

l) optionally postcrosslinking the reaction mixture obtained from k),

m) drying the reaction mixture obtained from k) or l), and

n) optionally grinding and/or sieving the reaction mixture obtained from k), l) or m).

20. A process for preparing a crosslinked hydrogel, comprising steps a) to i) as per any of claims 13 to 18 and additionally

k) polymerizing the reaction mixture from one of stages a) to i) if performed, with optionally additional monoethylenically unsaturated compounds N and optionally also at least one further copolymerizable hydrophilic monomer M in the presence of at least one free-radical initiator K and optionally of at least one grafting base L,

l) optionally postcrosslinking the reaction mixture obtained from k),

m) drying the reaction mixture obtained from k) or l), and

n) optionally grinding and/or sieving the reaction mixture obtained from k), l) or m).

21. Polymer obtainable according to a process as per either of claims 19 and 20.

22. Crosslinked hydrogel containing at least one hydrophilic monomer M in copolymerized form crosslinked with an ester F as per any of claims 1 to 12.

23. Crosslinked hydrogel containing at least one hydrophilic monomer M in copolymerized form crosslinked with a reaction mixture which contains ester F and is obtainable according to a process of claims 13 to 18.

24. Use of a polymer as per any of claims 21 to 23 in hygiene articles, packaging materials and in nonwovens.

25. A composition of matter comprising

- from 0.1% to 40% by weight of at least one ester F as per any of claims 1 to 12 and (meth)acrylic acid,
- 0.5 – 99.9% by weight of at least one hydrophilic monomer M,
- 0 – 10% by weight of at least one esterification catalyst C,
- 0 – 5% by weight of at least one polymerization inhibitor D, and
- 0 – 10% by weight of a solvent E,

with the proviso that the sum total is always 100% by weight.

26. A composition of matter as per claim 25, further comprising

- a diluent G ad 100% by weight.

27. Crosslinked hydrogel obtainable from a composition of matter as per claim 25 or 26 and additionally

l) optionally postcrosslinking the reaction mixture obtained,
m) drying the reaction mixture obtained directly or from l), and
n) optionally grinding and/or sieving the reaction mixture obtained directly or from l) or m).

28. Use of a reaction mixture obtainable according to any of claims 13 to 17 or of a composition of matter as claimed in claim 25 or 26

- as a free-radical crosslinker of water-absorbing hydrogels,
- as a starting material for preparing polymer dispersions,
- as a starting material for preparing polyacrylates,
- as a paint raw material, or
- as a cement additive.

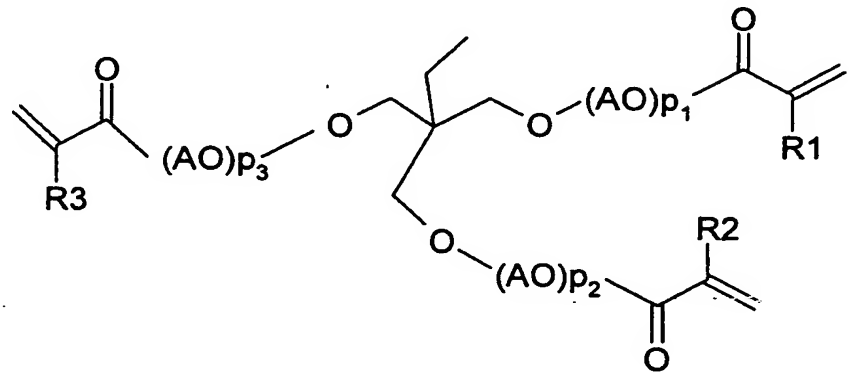
29. Crosslinked hydrogel as per any of claims 21, 22, 23 and 27 having a residual crosslinker content of less than 10 ppm, preferably less than 8 ppm, and more preferably less than 5 ppm.

30. Use of an ester F as per any of claims 1 to 12 for preparing hydrogel-forming polymers capable of absorbing aqueous fluids.

(Meth)acrylic esters of polyalkoxylated trimethylolpropane

Abstract

The present invention relates to novel (meth)acrylic esters of polyalkoxylated trimethylolpropane of the formula



where AO is for each AO independently at each instance EO, PO or BO

where EO is O-CH2-CH2-

PO is independently at each instance O-CH2-CH(CH3)- or O-CH(CH3)-CH2-

BO is independently at each instance O-CH2-CH(CH2-CH3)- or O-CH(CH2-CH3)-CH2-

p1 + p2 + p3 is 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74 or 75,

R1, R2 and R3 are independently H or CH3,

a simplified process for preparing these esters and the use of reaction mixtures thus obtainable.